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Full Length Article

Microstructure and microwave dielectric properties of $Na_{1/2}Sm_{1/2}TiO_3$ filled PTFE, an environmental friendly composites

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ABSTRACT

A study on $Na_{1/2}Sm_{1/2}TiO_3$ filled and glassfiber reinforced polytetrafluoroethylene (PTFE) composites was described. The GF content was a fixed value of 4 wt%, and the NST content in the composite matrix changed from 26 to 66 wt%. The paper consisted of the manufactural process of the composite and the effects of filler content on the properties of the substrate, such as morphology, moisture absorption, density, dielectric properties and temperature coefficient of dielectric constant. As NST filler loading increased from 26 to 66 wt%, the dielectric constant and loss tangent experienced a continuously increase while the development in τ_ε was opposite. X-Ray Diffraction, FTIR and XPS were used to analyze the microstructure of modified ceramic powder. It was proved that the silane coupling agent has been grafted on the NST surface successfully. At last, the NST/GF filled PTFE composites exhibited good dielectric constant (ε_r = 4.95), low dielectric loss (tan δ = 0.00147), acceptable water absorption (0.036) and temperature coefficient of dielectric constant (τ_ε = −164) at filler loading of 4 wt% GF and 46 wt% NST.

1. Introduction

Ceramic powder filled polytetrafluoroethylene (PTFE) has been widely used as base substrate for the fabrication of microwave devices. Some of their advantages over the conventional ceramic substrates are high solvent resistance, low moisture absorption, light weight, non-pollution, and low energy consumption [1]. However, the main disadvantage of filled PTFE are its low mechanical strength and high linear coefficient of thermal expansion (CTE = 109 ppm/°C. Therefore, micro-fiberglass(GF) and ceramic powders have been loaded as fillers to improve the mechanical strength and lower the CTE of the composites [2–6]. Prior, a lot of researches have been performed to illustrate the effects of various modified ceramic fillers on the electrical properties of PTFE/ceramic composites, such as silica (SiO_2) [7–9], alumina (Al_2O_3) [3], magnesia (MgO) [10] and $MgTiO_3$ [1]. The above mentioned composites exhibit a relatively low dielectric constant (ε_r) ranging from 2.9 to 4.3. It is well known that compositional variations in ceramic fillers, fillers particle sizes, distributions, processing techniques, etc. have significant influence on the microwave dielectric properties of the composite substrates. However, several researchers have evaluated the surface characterization of modified powders and the bonding mechanism between PTFE and fillers. Surface static water contact angle (CA), X-ray photoelectron spectroscopy (XPS) and peak fitting analyses were initially conducted to study the surface characterizations of fluorosilane treated ceramic fillers by Yang [11,12]. In our recent work [13–15], $Na_{1/2}Sm_{1/2}TiO_3$(NST) is an excellent microwave dielectric ceramic with a high dielectric constant ε_r = 100, a high quality factor Q × f = 10000 GHz, and an extremely low dielectric loss (tan δ = 0.0003). And the manufacture processes of both NST powder and NST/GF filled PTFE substrates are eco-friendly. Therefore, it is expected that NST/GF filled PTFE composite substrates also possess outstanding microwave dielectric properties.

In the present work, NST/GF filled PTFE composites with different filler fractions (30–70 wt%) were prepared. The content of GF in the PTFE matrix was a fixed value of 4 wt%. NST powders were prepared by the solid state ceramic route. GF and NST ceramic particulate fillers were coated with silane coupling agent before incorporating with PTFE to have much effective fillers and PTFE inter-coupling and also to prevent water absorption by the GF

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and ceramic fillers, which deteriorate the properties of the substrate [3,9]. Accordingly, a systematic study has been performed to investigate the microstructure and effect of NST filler loading on the dielectric properties, density, moisture absorption and temperature coefficient of dielectric constant (τ_ε) of the NST/GF filled PTFE composites. What's more, the mechanisms of modification and recombination processes were also described in details in this paper.

2. Experimental

2.1. Fabrication of NST powder

NST powder were prepared by the solid state ceramic route. Reagent grade powders of Na_2CO_3, Sm_2O_3 and TiO_2 were used as starting raw materials. According to the stoichiometric ratio, the Na_2CO_3, Sm_2O_3 and TiO_2 were weighed, mixed in alcohol and ball milled for 5 h. The dried powder was then calcined at 1300 °C for 2 h.

2.2. Fabrication of the NST/GF filled PTFE composite substrates

The calcined NST powder and GF (Huate, Shanxi) were used as filler, and loaded into the PTFE suspension (DISP30, Dupont, China). Table 1 gives the properties of raw materials. F8261 ($C_{14}H_{19}F_{13}O_3Si$, TCI Corporation, Japan) was used to modify NST and GF fillers.

In this work, F8261 was used as coupling agent to coat the surface of fillers. The methods to modify GF and NST particles were same. First, a certain amount of F8261 and pre-treated filler was weighted. Then, the coupling agent was hydrolyzed in ion-free water and alcohol at 55 °C for 1 h. The amount of F8261 was 1.5% of the weight of pre-treated filler and the amount of water was controlled exactly for the hydrolysis of F8261. Then the filler was added and dispersed into the hydrolyzed coupling agent solution by heavy stirring for 2 h. The slurry was further dried in an oven at 120 °C for 3 h and silane coupling agent treated filler was obtained.

Filler content of GF powder was a fixed value of 4 wt% in this experiment. And the content of NST in PTFE matrix varied from 26 wt% to 66 wt%. The GF and NST previously obtained were weighted accurately to prepare the composites according to the weight radio NST/GF/PTFE. The coupling agent treated GF and NST powders were added into the PTFE aqueous dispersion and mixed by heavy stirring for 3 h to obtain a fine mixture. The mixture was then dried at 120 °C for 24 h to eliminate water. The dried dough was smashed by a high speed pulverizer. The obtained composite powders were pressed into square slices (150 mm*150 mm*1 mm) by cold pressing. The slices were hot pressing sintered at 380 °C and 10 MPa. Hot treatment was performed in a program controlled oven. PTFE was melted and coalesced during hot treating, and then recrystallized while cooling.

2.3. Characterization studies

The density of the NST/GF/PTFE composites were measured by Archimedes' principle. The morphology of the GF, ceramic powders and the surface microstructure of the composites were obtained by scanning electron microscopy (SEM, model JEOL JSM-6490). Water absorption of the composite sample was measured as reported earlier by Murali etc. according to IPC-TM-650 2.6.2 [16].

The crystal phase of NST powder and substrate composite were identified by X-ray powder diffraction (XRD) using a Philips X'prt diffractometer. Fourier transform infrared spectra (FTIR) of F8261 and NST/GF/PTFE substrate were performed on a Nicolet FTIR 5700 spectrophotometer. X-ray photoelectron (XPS, AL, K-ALPHA, Thermo Scientific) was utilized to study the ceramic surface. All spectra were collected using Al-Kα radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot with a diameter of 500 μm. Survey scan of samples was conducted over a range of 1350 eV with a step size of 1 eV, 100 ms per step and 150 eV pass energy. In addition, a high resolution scan for detected elements was obtained at a step size of 0.1 eV in order to confirm chemical states of the elements present in the NST.

The dielectric constant (ε_r), dielectric loss (tan δ) and temperature coefficient of dielectric constant (τ_ε) of the composites of the substrates were measured by stripline resonator method using Agilent E8363A microwave network analyzer according to IPC-TM-650 2.5.5.5 specification [17]. The testing samples size were 20 mm width, 30 mm length and 1 mm in thickness. The testing frequencies covered the region from 7.0 GHz to 13.0 GHz. The ε_r and tan δ of the NST/GF/PTFE composites reported in this paper was at a frequency around 10 GHz.

Table 1
The properties of PTFE, NST and GF.

Properties	PTFE	NST	GF
Density/(g/cm3)	2.2	5.0	2.12
Dielectric constant	2.1	100	4.9
Dielectric loss	0.0003	0.0003	0.006
Thermal expansion coefficient/(10-6 K^{-1})	109	8	5.4

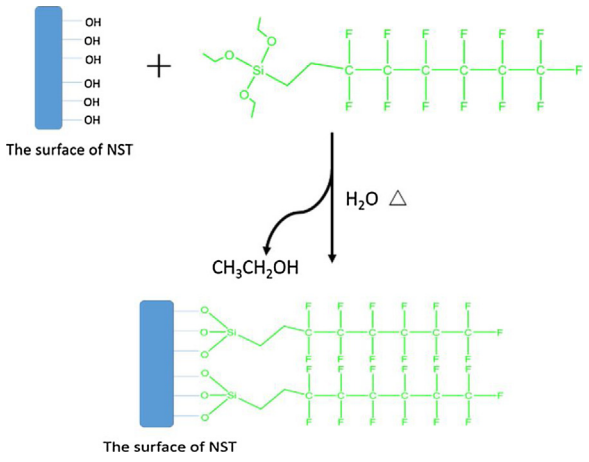
3. Results and discussion

3.1. Microstructure analysis

The crystal structure of NST ceramics is represented in Fig. 1. According to the structure, we found that $Na_{1/2}Sm_{1/2}TiO_3$ ceramic was crystallized as orthorhombic perovskite structure [13]. TiO_6 octahedra exist in the lattice formed by Na and Sm.

XRD analysis was used to confirm the phase purity of NST powder sintered at its optimal sintering temperature for 2 h in air. As shown in Fig. 2, the XRD pattern of NST powder was crystallized as orthorhombic perovskite structure and no secondary phases were detected throughout the whole scanning angles according to the analysis of powder XRD profiles [18,19]. The XRD spectrum of NST/GF filled PTFE substrate was also performed in Fig. 2, from which we could conclude that the NST filled PTFE composites were synthesized.

As shown in Scheme 1, F8261 reacted with hydroxyl of inorganic NST and modified ceramic was obtained. XPS analysis was performed to ascertain whether the F8261 has coated on the surface of ceramic fillers, as shown in Fig. 3. Survey scan of NST powders



Scheme 1. The schematic of F8261 reaction to produce the modified NST surface.